

**California Environmental Protection Agency**



# **Air Resources Board**

**PROCEDURE FOR  
ORGANIC CARBON AND ELEMENTAL CARBON (OC/EC) ANALYSIS  
OF VEHICULAR EXHAUST PARTICULATE MATTER (PM)  
ON QUARTZ FILTERS**

**Standard Operating Procedure No. MLD 139  
Version 1.0**

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## **SOP MLD 139**

### **PROCEDURE FOR ORGANIC CARBON AND ELEMENTAL CARBON (OC/EC) ANALYSIS OF VEHICULAR EXHAUST PARTICULATE MATTER (PM) ON QUARTZ FILTERS**

#### **1.0 SCOPE**

This document is a standard operating procedure (SOP) for organic carbon (OC) and elemental carbon (EC) analysis of vehicular exhaust particulate matter (PM) on quartz fiber filters using a Desert Research Institute (DRI) Thermal/Optical Carbon Analyzer (Analyzer).

#### **2.0 SUMMARY OF METHOD**

The method is based on the preferential oxidation of OC and EC at different temperatures and under different conditions. A 5/16 inch diameter sample is taken from a quartz filter deposited with vehicular exhaust PM, placed inside an Analyzer and heated to selected temperatures under selected conditions. At low temperatures and in a helium (He) atmosphere, OC is volatilized and removed from the quartz filter while EC is not. The volatilized OC is swept by helium over a hot oxidizer (manganese dioxide,  $\text{MnO}_2$ ) and converted to carbon dioxide ( $\text{CO}_2$ ). The  $\text{CO}_2$  is then reduced to methane ( $\text{CH}_4$ ) by passing the flow through a methanator (a nickel catalyst). A flame ionization detector (FID) is used to quantify the methane. After all OC is removed from the sample, the filter is further heated to higher temperatures in a controlled oxygen atmosphere. EC is pyrolyzed to  $\text{CO}_2$ , converted to  $\text{CH}_4$  and quantified with the FID. With an appropriate calibration factor, the amounts of OC and EC can be calculated from the FID peak areas.

To avoid underestimation of OC and overestimation of EC due to pyrolyzed OC, it is necessary to make a correction for the pyrolysis of OC to EC. To accomplish this, sample light reflectance and transmittance are continuously monitored via a helium-neon laser and photo detectors throughout an analysis cycle. As pyrolysis takes place, there is an increase in light absorption resulting in a decrease in reflectance and transmission. By monitoring the reflectance/transmittance, a pyrolytic correction (PC), the portion of the EC peak corresponding to pyrolyzed OC, can be accurately assigned to the organic fraction.

The analysis normally follows the IMPROVE\_A (Interagency Monitoring of Protected Visual Environments\_A) protocol. However, other protocols such as the IMPROVE or NIOSH (National Institute of Occupational Safety and Health) or STN (Speciation Trends Network) protocol can also be used.

#### **3.0 INTERFERENCES**

- 3.1 The presence of carbonate carbon presents significant interference in carbon analysis if it constitutes more than 5% of total measured carbon. Acid pretreatment of the filter samples will eliminate the carbonate interference (Section 11, Carbonate Analysis). In routine analysis, carbonate is not measured.

- 3.2 The presence of minerals and colored materials can affect the laser correction for pyrolysis:
- Some minerals change color as the sample filter is heated, generally resulting in a darker sample.
  - Some minerals may affect the laser reflectance by temporarily changing color or changing the surface texture of the deposit residue. These changes are reversible and highly temperature dependent.
  - Colored organic compounds can affect the laser correction causing increased reflectance as these compounds are removed.
  - The presence of certain elements (Na, K, Pb, Mn, V, Cu, Ni, Co, and Cr) as part of the deposit material has been shown to catalyze the removal of elemental carbon at lower temperatures.
- 3.3 Moisture on the filter can affect the FID baseline and peak area integration. An adequate delay time (Sections 8.1.2 and 10.13) for the sample filter to dry in the Analyzer by passing helium over the filter punch will eliminate this interference.
- 3.4 Sample filters exposed to dust can be contaminated by the PM in the environment. Using clean surfaces, storing filters in clean containers and handling filters carefully in a clean environment will minimize contamination.

#### 4.0 APPARATUS AND MATERIALS

- 4.1 DRI (Desert Research Institute) Thermal/Optical Carbon Analyzer Model 2001.
- 4.2 Quartz filters, 47 mm (Pall Corporation, Tissuquartz filter, Part No. 7202 (pre-heat-treated) or No. 7194 (non-heat-treated), and filter containers (Millipore Petrislide, Cat. No, PD1504700), or equivalents.
- 4.3 Steel punch tool, 5/16 inch diameter.
- 4.4 Glass petri dish or a glass plate with a flat surface, for cutting 5/16-in sample punch from filter with punch.
- 4.5 Tweezers, flat tip.
- 4.6 Thermolyne furnace, Model 30400.
- 4.7 Coors porcelain plates for firing quartz filters, 230 mm diameter, Coors # 60456.
- 4.8 Gases:
- (a) Compressed air for valves.
  - (b) Ultra zero air for FID.
  - (c) Hydrogen, from a hydrogen generator (Parker Balston H<sub>2</sub>-90, or equivalent) or from an ultra-pure hydrogen cylinder.
  - (d) 10% oxygen in helium, certified, Scott-Marrin, Inc, catalog # 02-150A-590B.
  - (e) Helium, Ultrapure, 99.9995%.
  - (f) 5% methane in helium (Cal Gas), traceable to NIST standards, Scott-Marrin, Inc., catalog # 02-150A-350B.
  - (g) 5% carbon dioxide in helium, traceable to NIST standards, Scott-Marrin, Inc., catalog # 02-150A-580B.

#### 4.9 Chemicals:

- (a) Potassium hydrogen phthalate (KHP), ultrapure (Spectrum Chemical, # P1960, or equivalent), CAS 877-24-7.
- (b) Sucrose, ultrapure (Spectrum Chemical, # S1697, or equivalent), CAS 57-50-1.
- (c) Manganese dioxide ( $\text{MnO}_2$ ), reagent, as an oxidizer in the oxygen oven (Spectrum Chemical, # M1107, or equivalent), CAS 1313-13-9.
- (d) Nickelous nitrate [ $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ], reagent, used as a reducer in the methanator (Spectrum Chemical, # N1062, or equivalent), CAS 13478-00-7.
- (e) Chromosorb 60/80 mesh, used as a support for nickel catalyst in methanator (Supelco, catalog # 2-0165, or equivalent). Both nickelous nitrate and Chromosorb are for preparing the reduction catalyst in the methanator.
- (f) Hydrochloric acid (HCl), concentrated, for preparing KHP reagent (Fisher Scientific, A466-500, or equivalent), CAS 7647-01-0.
- (g) Hydrochloric acid (HCl), 0.5 N, for carbonate analysis (Spectrum Chemical, # H-130, or equivalent).
- (h) Nanopure water.

#### 4.10 Gas purification traps:

- (a) Oxygen trap for helium.
- (b) Hydrocarbon trap for helium.
- (c) Moisture trap for hydrogen.

#### 4.11 Syringes:

- (a) Gas-tight syringes, 500  $\mu\text{L}$ , 1000  $\mu\text{L}$  and 2500  $\mu\text{L}$  (SGE, P/N 007200, 008100, and 008500, respectively, or equivalents).
- (b) Liquid syringe, 25  $\mu\text{L}$  (Hamilton, P/N 80400, or equivalent).

#### 4.12 Volumetric flasks, 100 mL.

#### 4.13 FID flame igniter.

### 5.0 PREPARATION OF FILTERS

Quartz filters must be pre-fired to remove any traces of carbon compounds before use.

- 5.1 Visually inspect all quartz filters for damage. Place a batch of inspected filters on Coors porcelain plates using tweezers.
- 5.2 Place the porcelain plates and filters inside the oven of a Thermolyne 30400 Furnace oven.
- 5.3 Set the oven to heat to 900°C.
- 5.4 When oven temperature has reached 900°C, bake the quartz filters for four hours at 900°C (CAUTION: Do not open the hot furnace door as this can cause serious bodily injuries.)
- 5.5 Set oven temperature to room temperature and let the oven and filters cool down to room temperature.

- 5.6 Remove porcelain plates with the filters from the oven. Remove filters with tweezers and place each filter into an individually labeled filter container. Be careful not to damage any filters.
- 5.7 Place the filters and containers in a desiccator or a refrigerator for storage until use.
- 5.8 After pre-fire treatment, choose any random filter and analyze for OC and EC concentrations. The filter must have OC < 2.0 µgC/cm<sup>2</sup> and EC < 0.5 µgC/cm<sup>2</sup>. If the carbon concentrations are over the above limits, analyze one more filter. If the second filter also has carbon concentrations over these limits, all filters from the same batch must be discarded.

## 6.0 PREPARATION OF STANDARDS

- 6.1 The following four standards are used to calibrate the Analyzer:

- (1) Cal Gas (5% CH<sub>4</sub> in helium).
- (2) 5% CO<sub>2</sub> in helium.
- (3) Potassium hydrogen phthalate (KHP) solution.
- (4) Sucrose solution.

The gaseous standards are commercially available from Scott-Marrin (Section 4.8). The KHP and sucrose solutions are prepared as follows.

- 6.2 KHP standard solution

- 6.2.1 Dry KHP at 110°C for two hours before preparation of a solution.
- 6.2.2 After the KHP has cooled to room temperature, weigh and transfer 0.3826 g of KHP into a clean, dry 100-mL volumetric flask.
- 6.2.3 Dissolve the KHP in the flask with about 50 mL nanopure water.
- 6.2.4 Add 0.2 mL of concentrated HCl and dilute to volume with nanopure water.
- 6.2.5 Mix the KHP solution thoroughly. This will make an 1800 ppm carbon (or 1.80 µgC/µL) solution of KHP.
- 6.2.6 Label the flask and store the KHP solution in a refrigerator until needed. Do not freeze solution. This solution is good for 40 days.
- 6.2.7 The actual concentration of the KHP solution is calculated by:

$$\text{Actual } \mu\text{gC}/\mu\text{L} = \left( \frac{\text{wt of KHP}}{\text{vol of solution}} \right) \left( \frac{\text{no of carbon in KHP} \times 12}{\text{mol wt of KHP}} \right)$$

$$= \left( \frac{\text{wt of KHP in g}}{100 \text{ mL}} \right) \left( \frac{8 \times 12}{204.23} \right) \left( \frac{10^{-3} \text{ mL}}{\mu\text{L}} \right) \left( \frac{10^6 \mu\text{g}}{\text{g}} \right)$$

### 6.3 Sucrose standard solution

- 6.3.1 Weigh and transfer 0.4280 g of sucrose into a clean, dry 100-mL volumetric flask.
- 6.3.2 Dissolve sucrose in nanopure water and dilute to volume. Mix thoroughly. This will make an 1800 ppm carbon (or 1.80 µgC/µL) solution of sucrose.
- 6.3.3 Label the flask and store the sucrose solution in a refrigerator until needed. Do not freeze solution. This solution is good for 40 days.
- 6.3.4 The actual concentration of the sucrose solution is calculated by:

$$\begin{aligned} \text{Actual } \mu\text{gC}/\mu\text{L} &= \left( \frac{\text{wt of sucrose}}{\text{vol of solution}} \right) \left( \frac{\text{no of carbon in sucrose} \times 12}{\text{mol wt of sucrose}} \right) \\ &= \left( \frac{\text{wt of sucrose in g}}{100 \text{ mL}} \right) \left( \frac{12 \times 12}{342.31} \right) \left( \frac{10^{-3} \text{ mL}}{\mu\text{L}} \right) \left( \frac{10^6 \mu\text{g}}{\text{g}} \right) \end{aligned}$$

### 6.4 Blank solution

Prepare a blank solution using the same procedure as in Sections 6.2 or 6.3 without KHP or sucrose.

### 6.5 KHP solution for MDL determination

Transfer 2.5 mL of the 1800 ppm carbon KHP solution (Section 6.2) into a clean dry 100 mL volumetric flask. Dilute with nanopure water to 100 mL. This makes a 45 ppm carbon KHP solution, or 0.045 µg carbon per µL solution.

## 7.0 ANALYZER START-UP

### 7.1 Set temperatures

If the Analyzer is turned on for the first time, or after an extended period of non-operation, it will take a period of conditioning to reach a stable system background. At the start, allow all gases to purge through the system for about 15 minutes before heating various zones in a stepwise manner. Allow the FID and line heater to reach operating temperatures before heating up the oxygenator and methanator. Using the Watlow Controllers, set temperatures of FID, line heater, oxygenator and methanator as follows:



FID: 200°C.  
 line heater: 105°C.  
 oxygenator: 900°C (heat up stepwise in ~100°C increments with at least ~30 min. holding time at each temperature).  
 methanator: 420°C (heat up stepwise in ~100°C increments with at least ~30 min. holding time at each temperature).

## 7.2 Set gas flows

- 7.2.1 Check all gas cylinder pressures. Cylinders with gas pressures less than 500 psi should be replaced before beginning the day's analysis.
- 7.2.2 Turn the analysis mode select switch (front left upper corner) to "Analyze" position. After the sample boat has moved inward and the inlet breech has closed, adjust rotameters to the values posted on each individual rotameter. These values are factory calibrated to give the following gas flow rates at the following pressures. (Reference 14.1, Analyzer Operation Manual, pp. 22-24)

Cylinder regulator pressures (psi):

Cal Gas	20
He/O <sub>2</sub> , CO <sub>2</sub> /He, air and H <sub>2</sub>	15
He	25
Pneumatic air	25

Gas flow rates (mL/min):

He-1	40
He-2	10
He-3	50
He/O <sub>2</sub>	10
Air	350
H <sub>2</sub>	35
Cal Gas	~10-20

- 7.2.3 Set H<sub>2</sub> flow to the higher posted value on the H<sub>2</sub> rotameter. Wait for the flow to stabilize. Light the FID with a flame ignitor. After several minutes, set the H<sub>2</sub> rotameter to the lower posted value. On Analysis Setup page, set FID ID to "FID\_8" and polarity to "Unipolar". Use "FID\_6" only for the very heavily loaded samples.

## 7.3 System leak check

- 7.3.1 Check system gas leaks in accordance with the Analyzer Operation Manual, p. 27 (Reference 14.1).
- 7.3.2 Allow FID, line heater, oxygenator and methanator to reach operating temperatures.
- 7.3.3 The two toggle shut-off valves in conjunction with the System Oven Pressure digital panel meter (DPM) located on front of the instrument above the rotameters are used for detecting gas leaks in the Analyzer. The Oven Outlet toggle valve is located on the right side panel. The Oven Inlet toggle is on the front of the instrument.

- 7.3.4 Make sure that He-1, He-2, and the pneumatic air are flowing and that the bridge of the sample boat inlet is sealed. If not, manually switch the sample boat to "Calibrate" to ensure the bridge is sealed.
  - 7.3.5 Close (flip down) the Oven Outlet toggle valve. The Sample Oven Pressure should increase. When the pressure reaches about 5 psi, close the Oven Inlet toggle (flip down). The pressure should not decline very much over one minute; if it does, there may be a leak. Normally, the most likely leaks are the Teflon ferrules around the thermocouple push rod and the quartz oven inlet and outlet. Tightening the nut should stop the leak. Also, check the septum ports. The two remaining areas are the top and bottom seals of the quartz oven cross. If the leak persists, the oven may have a crack. (Caution: Over tightening the nuts and ferrules may crack the quartz components.)
  - 7.3.6 When the system leak checks are satisfactory, open the toggles to re-establish flow.
- 7.4 Balance gas flows
- Balance gas flows by adjusting the three needle valves on the Analyzer's right side panel in accordance with the Analyzer Operation Manual, pp. 27-28 (Reference 14.1).
- 7.4.1 Make sure that the sample boat inlet bridge is closed, and that the flow rates have been set correctly and all the gases are flowing.
  - 7.4.2 Make sure FID, line heater, oxygenator and methanator are at the operating temperatures.
  - 7.4.3 Using the Carbon Analysis program\Manual\Control, turn on the Back Valves. Fully open (counter-clockwise) the Sample Oven Flow Adjust needle valve (on the right side panel) and note the System Oven Pressure meter reading on the front panel. Adjust the Sample Oven Flow Adjust needle valve (clockwise) to increase the pressure by approximately 0.5 psi. Slightly higher or lower pressures are not critical. Allow the pressure to stabilize and record this reading.
  - 7.4.4 Turn off the Back Valves and adjust the Vent Adjust needle valve (on the right side panel) to the same Sample Oven Pressure reading as recorded in Section 7.4.3. Turn the Back Valves on and off several times to see that there is no fluctuation in the System Oven Pressure reading. Leave the Back Valves on for the next step.
  - 7.4.5 Turn on the Front Valves and note the absence of ball movement at the He-2 rotameter. If the ball jumps up, turn the He/HeO<sub>2</sub> adjust needle valve clockwise slightly. If the ball drops, turn the needle valve counter-clockwise.
  - 7.4.6 Turn off the Front Valves and let the flow stabilize. Repeat steps in Section 7.4.5 until little or no ball movement at the He-2 rotameter is observed.
  - 7.4.7 The default setting is with Back Valves closed and Front Valves open.

### 7.5 Start carbon analysis software

Set mode selector to "Analyze" (upper left corner of front panel). Double click the DriCarb.exe or double click the shortcut of DriCarb.exe to begin the Carbon Analysis program. The DRI carbon analysis "Welcome" page will appear. Then set mode selector to "Auto". Click "Analysis" on the "Welcome" page to bring up the "Setup" page and to begin carbon analysis.

## 8.0 CALIBRATION

There are three types of calibration: an annual calibration to verify the calibration factor, a routine daily calibration to verify performance of Analyzer, and an end-of-run calibration for FID peak area quantitation.

### 8.1 Annual calibration

The instrument is calibrated every year, or when the gas standard is changed, or when the catalysts are replaced, or when the instrument has a major service. The following four standards are used to calibrate the instrument: 5% CH<sub>4</sub> in helium (Cal Gas), 5% CO<sub>2</sub> in helium, KHP solution and sucrose solution. At the end of each analysis a 1-mL sample of the Cal Gas is also automatically injected by a Carle valve (in a constant temperature compartment) and is used as the internal standard. During calibration, the same Cal Gas is used for dual purposes: as the internal standard and as the analyte manually injected in different quantities.

#### 8.1.1 Calibration with gaseous standards

Select "Analysis" from Welcome page. Under "Type" drop down menu, choose "Calib". In the "Command" drop down table, select "cmdCalib-HeO<sub>2</sub>". Select "Methane" in the "Cal Gas" box and "Helium" in the "Carrier Gas" box. Enter record keeping information. Click "OK" to start. When prompted "Please load gas syringe", load syringe with Cal Gas or CO<sub>2</sub> in the following volumes (μL):

<u>Volume</u>		<u>Carbon conc</u>
100 μL	(using a 500 μL syringe)	2.68 μg C
250 μL	(using a 500 μL syringe)	6.70 μg C
500 μL	(using a 1000 μL syringe)	13.4 μg C
1000 μL	(using a 1000 μL syringe)	26.8 μg C
1500 μL	(using a 2500 μL syringe)	40.2 μg C

When prompted for injection, inject sample through the injection port. At STP, for the 5% CH<sub>4</sub> Cal Gas or the CO<sub>2</sub> gas, the carbon concentration is 0.0268 μg C/μL. This gives a series of carbon concentrations as shown above. Depending on the CH<sub>4</sub> or CO<sub>2</sub> certified concentrations provided by the standards manufacturer, the actual carbon concentrations can be calculated. These carbon concentrations are then corrected for the temperature and pressure at the laboratory using the following formula derived from the Ideal Gas Law:

$$A_{\text{actual}} \mu\text{g C}/\mu\text{L} = \left( \frac{P_a}{760} \right) \left( \frac{1}{(T + 273.15)} \right) \left( \frac{1}{0.08206} \right) \left( \frac{\% \text{ conc of gas}}{100} \right) \times 12$$

where  $P_a$  is the atmospheric pressure in mm Hg and  $T$  is the room temperature in °C. Divide the  $\text{CH}_4$  or  $\text{CO}_2$  peak area by the internal standard peak area to obtain the peak area ratio for the corresponding carbon concentration ( $\mu\text{g C}$ ).

#### 8.1.2 Calibration with KHP and sucrose standard solutions

Select "Analysis" from the "Welcome" page. Under "Type" drop down menu, choose "Analysis". Complete record keeping information. Bake quartz boat and oven at 900°C for 10 min. using "cmdBakeOvenARB" (or an equivalent protocol) from the Command Table. After baking, select "cmdImproveA" (or an equivalent protocol) from the Command Table. Enter record keeping information such as solution volumes and concentrations. After the oven has cooled to below 50°C, the quartz boat moves out of the quartz tube to allow sample loading. Using a 25  $\mu\text{L}$  syringe, inject the standard solution in the following volumes onto the filter punch:

<u>Volume</u>	<u>Total Carbon conc</u>
5.0 $\mu\text{L}$	9.00 $\mu\text{g C}$
10.0 $\mu\text{L}$	18.0 $\mu\text{g C}$
15.0 $\mu\text{L}$	27.0 $\mu\text{g C}$
20.0 $\mu\text{L}$	36.0 $\mu\text{g C}$

For the exactly 0.3826 g of KHP standard solution (Section 6.2) and 0.428 g of sucrose standard solution (Section 6.3), these injected volumes give a series of carbon concentrations as shown above. Depending on the actual concentrations of the KHP and sucrose solutions, the actual carbon concentrations can be calculated. The filter must be dried before analysis starts. Set "Delay of Start Run" time to allow at least one minute per  $\mu\text{L}$  of solution deposited. For a 10  $\mu\text{L}$  solution, for example, enter 600 seconds. After each analysis, add peak areas of all fractions (OC1 + OC2 + OC3 + OC4 + EC1 + EC2 + EC3) and divide by the  $\text{CH}_4$  internal standard peak area to obtain the area ratio for the corresponding carbon concentration ( $\mu\text{g C}$ ).

8.1.3 Repeat the above injection procedure (Section 8.1.2) using the blank solution (Section 6.4) with the same injection volumes. Add peak areas of all fractions (OC1 through EC3). If the peak areas from the blanks (normally around system blank level) are significant when compared to the peak areas of the corresponding volumes of standards, subtract the blank areas from the areas of the standard peaks before calculating the peak area ratios.

8.1.4 For each of the four calibrations, plot calculated carbon concentrations in  $\mu\text{g}$  carbon (y-axis) versus area ratios or corrected area ratios (x-axis). Force the curves through the origin and calculate the four slopes. Calculate the average value of the four slopes. These four slopes must be within  $\pm 20\%$  from the average slope. Enter the average slope into the Carbon.par file (third line: calibration slope), and the new value will become the current calibration factor, representing the Analyzer's response to generic carbons, efficiencies of the oxygenator and methanator and the sensitivity of the FID. The new response factor is normally within  $\pm 20\%$  of the previous value unless major Analyzer changes have been made.

## 8.2 Routine daily calibrations

Routine daily calibrations are to be performed at the beginning and at the end of each analysis day using Cal Gas standard and the automatic routine calibration command "cmdAutoCalib" in the command table. The automated calibration uses the Carle valve to inject the Cal Gas standard three times: first in a He-only atmosphere (peak 1), then in a He/O<sub>2</sub> atmosphere (peak 2), and finally, the normal calibration peak at the end of analysis (peak 3). These three peaks should have identical or very similar peak areas if the conditions of the catalysts are good and the calibration factor holds. Use the following steps to perform this automated calibration.

8.2.1 From the "Welcome" page, select "Analysis".

8.2.2 Set Type to "Sample" and select "cmdAutoCalib" from the drop-down menu in the "Command table" field.

8.2.3 Enter "Calib" for project name and "CalibYYMMDD" for sample ID, where YYMMDD is the year, month and date for the day of analysis.

8.2.4 Enter the Run # "1" for first calibration of the day and "2" for second calibration of the day, etc. Enter "1" in the "Punch area" and "Deposit area" fields. Set the Cal Gas flow rate to ~10-20mL/min. Click "OK" and "Run".

8.2.5 After the run, review the thermogram and record the three peak area counts in the log book and in the control charts (Section 13-3). The three peak area counts should be above 20,000 and must be within  $\pm 20\%$  of one another. The area of peak 3 (Cal Gas) should also be within  $\pm 20\%$  of the Cal Gas peak areas of other runs.

## 8.3 End-of-run calibration

The carbon analysis program uses the internal standard calibration method to quantify all FID peaks. At the end of each analysis, the Carbon Analysis program automatically injects a set quantity of Cal Gas (the internal standard). All FID peak areas are normalized to the Cal Gas peak area to minimize the effects of FID performance and electronic drift over time. The end-of-run calibration occurs automatically at the end of each analysis and requires no operator's intervention. After each run, the Cal Gas peak area count should be checked and compared to the Cal Gas peak area counts from previous runs. If the area count is within  $\pm 20\%$  from previous counts, the Analyzer is considered operating properly.

8.4 Currently there is no NIST-traceable primary standard available for carbon analysis. The current calibration procedure is for the total carbon, and there is no existing routine procedure to check the accuracy of the OC/EC split.

## 9.0 MINIMUM DETECTION LIMIT

The Analyzer's minimum detection limit (MDL) is determined initially during method development and verified during annual calibration, or after a major repair that affects performance of the Analyzer. The MDL applies to the Analyzer's operation only and does not take into account any other variables during sample collection process. Therefore, when interpreting the Analyzer's OC/EC data, consideration must be given to these other variables.

- 9.1 The MDL is determined by analyzing seven replicates of a 0.45 µg carbon per µL KHP standard solution (Section 6.5).
- 9.2 Using a 25 µL syringe deposit a 10-µL aliquot of the KHP standard solution onto a clean baked filter punch on the quartz boat, and the sample is analyzed using "cmdImproveA". Calculate the sum of all peak areas (OC1 + OC2 + OC3 + OC4 + EC1 + EC2 + EC3). Check and make sure the calibration peak area at the end of run is within limits.
- 9.3 Repeat this procedure (Section 9.2) for a total of seven times.
- 9.4 Calculate the standard deviation for all seven runs.
- 9.5 The MDL is the standard deviation times the student T value, 3.143, for seven replicates.
- 9.6 The Analyzer's manufacturer has reported that DRI has determined a MDL of total carbon 0.93 µg/cm<sup>2</sup>. The value was based on the analyses of 693 individual quartz filters at DRI and MDL defined as three times the standard deviation of their measured results (Ref.1, Analyzer Operation Manual, p 32). Using procedure as described above, our determined value is 0.62 µg/cm<sup>2</sup>.

## 10.0 ROUTINE OC/EC ANALYSIS

- 10.1 The OC/EC analysis normally follows the IMPROVE\_A protocol using the "cmdImproveA" command in the command table. Other analysis protocols in the command table may also be used.
- 10.2 Make sure the printer is on and in proper working condition. A report will be printed out after each analysis is completed.
- 10.3 Check all gas flow rates and pressures (Section 7.2). Verify sample oven pressure reading. If hydrogen generator is used, check water level on the hydrogen generator and add water if needed.
- 10.4 Set H<sub>2</sub> flow to the higher setting as posted on the rotameter (approximately 4.4). Let the flow stabilize. Light the FID with a flame ignitor. After several minutes, set the H<sub>2</sub> rotameter to the marked operating setting (approximately 3.4).
- 10.5 Leak test the system (Section 7.3).
- 10.6 Balance the gas flows if necessary (Section 7.4).
- 10.7 On the computer, double click the "DRICarb" shortcut icon to start the carbon analysis program.
- 10.8 Bake the oven using the "cmdBakeOvenARB" command. This can be done by clicking the "Analysis" button on the "Welcome" page, selecting "Sample", then "cmdBakeOvenARB". Enter record keeping information. Click "OK" and "Run". Repeat the bake oven procedure if necessary. No data is collected during this run.
- 10.9 After running "cmdBakeOvenARB", run a system blank using "cmdSysBlankARB" to ensure the system is clean. The system blank should have total carbon concentration < 0.3 µg/cm<sup>2</sup> before analyzing any samples. If not, repeat Sections 10.8 and 10.9 until system blank total carbon concentration is < 0.3 µg/cm<sup>2</sup>.

- 10.10 Once the system is confirmed clean, perform routine daily calibration using the "cmdAutoCalib" command to verify the Analyzer's performance (Section 8.2). If the total carbon concentration values are within limits, sample analysis can proceed.
- 10.11 Make sure the tweezers, the punching tool, and the glass surface area used to punch on are thoroughly wiped clean with a dry kimwipe.
- 10.12 Enter sample record keeping information on the "Setup" page. For a 5/16 in. punch, enter 0.50 (cm<sup>2</sup>) on "Punch area". Measure the inside diameter of the filter holder (if measurement is not available, measure the diameter of the circular deposit area on the filter) in cm (Section 10.16) and calculate the deposit area in cm<sup>2</sup> using the formula  $\text{Area} = \pi r^2$  where r is the radius in cm. Enter this value (usually about 12) in the field "Deposit area". Remove filter from container with tweezers to a clean glass petri dish or a flat glass surface. Visually inspect filter. Reject any filter if physical damage or non-uniformity or unusual deposit is found. Gently push down a 5/16 inch punch on filter to cut a disc. Remove the cut filter punch with tweezers and place on the quartz boat with the loaded surface facing up. Return the filter to the container for storage or additional analysis.
- 10.13 After loading sample punch, click "OK". When prompted for "delay time", enter the appropriate delay time and click "OK". The default value of delay time is 90 seconds and is applicable to most analysis unless the sample has a high moisture content. After the delay time, the analysis will go through the sample analysis cycle.
- 10.14 Wipe the tweezers, petri dish, and punching tool with a clean kimwipe, and return the sample with the petri dish to the refrigerator.
- 10.15 Log sample ID, date sampled, site name, date analyzed, chemist initials, and other pertinent information in the lab notebook.
- 10.16 At the end of the analysis, a three-page report will be printed out which includes the FID peak areas, calculated OC, EC and TC concentrations (in µg carbon per cm<sup>2</sup> and in µg carbon per filter), and the thermogram. Examine the thermogram for proper laser response, temperature profiles, realistic carbon peaks, and the presence of the calibration peak at the end of the analysis.
- It should be noted that the reported carbon concentrations per filter is calculated based on the value entered in the "Deposit area". The circular boundary of the deposit area is never a clear-cut boundary, and so the accuracy of the reported values of carbon concentrations per filter is highly dependent on the accuracy of the deposit area determination. For consistency purposes, measure the inside diameter of the filter holder and use this value to calculate the deposit area. (Section 10.12)
- 10.17 Run a replicate analysis for every ten samples. Take a second filter punch from the same filter and analyze it in the same way. (Section 13.2)
- 10.18 Once all samples are analyzed for the day, perform end of the day calibration using "cmdAutoCalib" command and record the three peak area counts in log book. Any values outside the expected ranges should be investigated (Section 8.2). Re-analyze samples with questionable results if necessary.
- 10.19 At the end of the day, put the Analyzer on standby. Shut off the toggle valves on the instrument for He1, He2 and Cal Gas and close the respective gas supply valves. Leave the FID on.

## 11.0 CARBONATE ANALYSIS

- 11.1 Follow the steps in Routine OC/EC Analysis (Section 10) until the sample punch is loaded into the quartz boat (Section 10.12). Turn the selector to "Calibrate" and the sample punch automatically centers itself under the acid injection port. The computer will prompt you to inject the HCl.
- 11.2 Enter the Sample ID and other record keeping information. Select "cmdCarbonate\_Run1st" from the "Command" table drop-down field to start the analysis program.
- 11.3 Flush a 25- $\mu$ L syringe with 0.5N hydrochloric acid (HCl) into a waste beaker. When prompted to inject HCl, through the injection port, deposit 20  $\mu$ L HCl onto the filter punch, ensuring that the needle bevel is turned toward the punch and that the needle tip is touching the top of the punch.
- 11.4 When the analysis is underway, flush the syringe with nanopure water to prevent corrosion of the syringe plunger.
- 11.5 After the analysis is completed, the data system prints out a tabular summary and a thermogram. Select "cmdCO3Improve\_Run2nd" from the "Command" drop-down field and click "OK" and "Run". The program then automatically cycles into the normal OC/EC analysis, using the same Sample ID. Heat from the oxidation oven will dry the sample in this position (for approximately 20 minutes) without prematurely baking carbon from the sample, and the sample temperature should be in the 40°C's. When the punch is dry, the data system will start the normal OC/EC analysis. With "cmdCO3Improve\_Run2nd" in the run table, the analysis proceeds with the IMPROVE protocol. To run Improve\_A protocol in carbonate analysis, the temperature settings in the "cmdCO3Improve\_Run2nd" will need to be modified.

## 12.0 PROGRAM SOFTWARE

- 12.1 The OC/EC analysis program reads command sequences from and writes data to an Access database file. This file is C:\Carbon\Access\carbon.mdb. Double clicking on the "DriCarb" shortcut icon will open this file to start the carbon analysis program and the "Welcome" page.
- 12.2 The parameter file, carbon.par, is an ASCII file which contains specific analyzer information. This is where the calibration slope can be entered. Double clicking the "Carbon.par" will open this file. Be careful about changing any parameters in this file because any change in this file will affect performance of the Analyzer.
- 12.3 The command tables are in Microsoft Access. Each command table has all the steps for the analysis protocol. They contain all the information for operating the Analyzer during analysis.
- 12.4 While inside the Carbon Analysis program, closing any window will terminate the analysis program and the ongoing analysis. Instead, use "Exit" to return to the previous window. Also, click "Exit" to exit the Carbon Analysis program.



## 13.0 QUALITY CONTROL

### 13.1 Analyzer performance

- 13.1.1 System blanks are performed at the beginning of each analysis day to confirm the system is clean. (Sections 10.8 and 10.9)
- 13.1.2 Calibration with Cal Gas at the beginning and the end of the day verifies the condition of the Analyzer including the catalysts. (Sections 8.2, 10.10 and 10.18)

### 13.2 Repeatability

Run a replicate analysis for every ten samples. A second filter punch is taken from the same filter and analyzed (Section 10.17). The total carbon concentrations from the two runs are compared. The values should meet the following criteria:

<u>TC concentration</u>	<u>Criteria</u>
$< 10 \mu\text{g}/\text{cm}^2$	$< \pm 2.0 \mu\text{g}/\text{cm}^2$
$\geq 10 \mu\text{g}/\text{cm}^2$	$< \pm 20 \% \text{ of average of replicates}$

Replicates which do not meet these criteria must be investigated for Analyzer or sample anomalies. Analyzer anomalies include poor instrument response (as reflected in the calibration peak areas) or poor laser signals (affecting the splits between OC and EC). Typical sample anomalies are inhomogeneous deposits on filter and filter contamination from sampling or during analysis. Re-run replicates if a reason cannot be found.

### 13.3 Control Charts

Control charts are updated on each analysis day. Three control charts are plotted using the three peak areas in the beginning-of-the-day "cmdAutoCalib" run (Sections 8.2 and 10.10).

- 13.3.1 The first chart plots: (1) the area of peak 3 (Sections 8.2 and 10.10) and (2) the percent deviation of this peak area from a historical mean of the same peak area versus date of analysis.
- 13.3.2 The second chart plots: (1) area of peak 1 and (2) the percent of deviation of this peak area from a historical mean of the same peak area versus date of analysis.
- 13.3.3 The third chart plots: (1) area of peak 2 and (2) the percent of deviation of this peak area from a historical mean of the same peak area versus date of analysis.

- 13.3.4 The first control chart monitors the overall condition of the Analyzer including the FID, and the second and the third control charts monitor the conditions of the catalysts. Instances where any of these peak areas deviate by more than  $\pm 20\%$  from their historical means must be investigated and the cause must be corrected. The historical mean covers the previous three months' data and is updated monthly, or when the methane calibration gas is changed, or when the catalysts are replaced, or when extensive repairs are performed. Normally the Analyzer's catalytic efficiencies and FID response will decrease with time and the peak areas will also decrease. The control charts monitor these changes.

## 14 REFERENCES

- 14.1 DRI Model 2001 OC/EC Carbon Analyzer Installation and Operation Manual, Atmoslytic Inc, December, 2004.
- 14.2 Standard Operating Procedure for Organic and Elemental Carbon Analysis of Exposed Quartz Microfiber Filters, SOP MLD 065, California Environmental Protection Agency, Air Resources Board, July 29, 2002.
- 14.3 DRI Model 2001 Thermal/Optical Carbon Analysis (TOR/TOT) of Aerosol Filter Samples – Method IMPROVE\_A, DRI SOP #2-216.1, November 2005.